Investigating the δ/α′ Martensitic Phase Transformation in Pu-Ga Alloys

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Introduction and Motivation

The δ/α′ phase transformation in Pu-Ga alloys is unique and scientifically interesting

"Western" phase diagram — Russian phase diagram

Pu exhibits 6 solid phases at ambient pressure

Small amounts of Ga stabilize the δ phase indefinitely at ambient temperatures

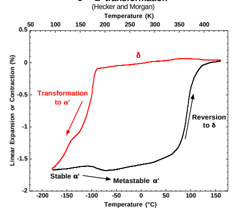
Russian work indicates that in 2-9% Ga alloys, a eutectoid transformation occurs – a 2 phase mixture of α + Pu_3Ga is stable at ambient temperatures

There is a martensitic phase transformation from δ to α′ at low temperatures

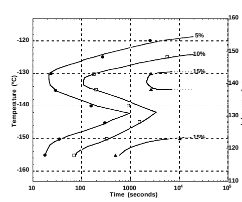
The δ ↔ α′ transformation has unusual characteristics

- Large hysteresis (90°C)
- Large volume change (20%)
- Incomplete transformation
- Double "C-curve" kinetics
- Martensitic transformation?
- Massive transformation? (Orme & Faires, 1975)

Continuous cooling dilatometry trace showing δ ↔ α′ transformation
(Hecker and Morgan)

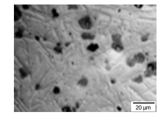


TTT curve for a 0.56 wt% Pu-Ga alloy
(Orme and Faires, 1975)

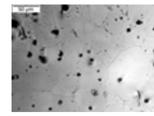


We are investigating the thermodynamics and kinetics of this transformation

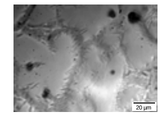
- Differential Scanning Calorimetry
  - Transformation temperatures, heats of transformation
- Resistivity
  - Transformation temperatures, extent of transformation
- Optical microscopy
  - Morphology, extent of transformation
- Transmission electron microscopy
  - Crystallographic relationships



0.6 wt% Pu-Ga alloy quenched to -120°C (nose of the upper "C" curve) and held for 10 hours



Untransformed grains of δ Pu-Ga alloy are equiaxed with an average grain size of ~50 μm

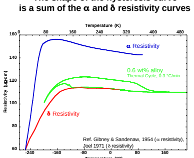


0.6 wt% Pu-Ga alloy quenched to -150°C (nose of the lower "C" curve) and held for 10 hours

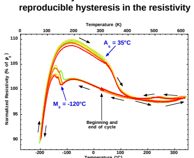
Experimental Results

Resistometry is used to characterize M_s and A_s temperatures and to determine the amount of transformation

The shape of the hysteresis curve is a sum of the α and δ resistivity curves



Thermal cycles at 1.5°C/min show a reproducible hysteresis in the resistivity



Unlike most metals, the resistivities of both the α and δ phases of Pu increase at intermediate temperatures before falling off sharply at low temperatures

α resistivity is 30% higher than δ at ambient temperatures

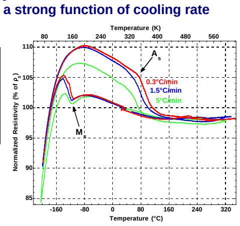
In the resistivity curve of the reference alloy, the distinct positive deviation from the δ resistivity curve indicates the beginning of α′ formation (M_s)

Maximum amount of transformation to α′ is ~26%

Resistivity cycles at different rates indicate that M_s is not a strong function of cooling rate

Cooling Rate (°C/min)	M_s (°C)	M_s (K)
0.3	-113	160
1.5	-116 to -123	150 to 157
5	-116	157

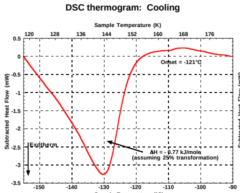
Hysteresis ≈ 150 K



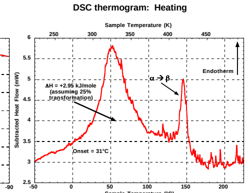
Numerous thermal cycles show reproducible M_s and A_s temperatures

Differential scanning calorimetry shows evidence of transformation on heating and cooling

DSC thermogram: Cooling



DSC thermogram: Heating



Transformation temperatures seen with DSC correlate well with those observed in resistivity experiments

Modeling the Hysteresis

Modeling begins with a thermodynamic analysis of the δ ↔ α′ transformation

At equilibrium $(=T_0), G_{a'} = G_d$, and

$$\Delta G_0^{\delta\to\alpha'} = (\Delta E_{\text{chemical}}^{\delta\to\alpha'} - T\Delta S^{\delta\to\alpha'} - P\Delta V^{\delta\to\alpha'}) = 0.$$

But, the transformation requires elastic and plastic work, and the second law can be written as:

$$\Delta G_{\text{specimen}} = (\Delta E_{\text{chemical}} - T\Delta S - P\Delta V) + (\Delta E_{\text{elastic}} + \Delta Q_{\text{plastic}}) < 0.$$

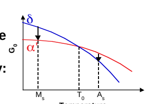
Since $P_{atm}\Delta V << \Delta E_{\text{elastic}}$,

$(\Delta E_{\text{chemical}} - T\Delta S) < (-\Delta E_{\text{elastic}} - \Delta Q_{\text{plastic}})$, and therefore

$$T_0 - M_s \cong \frac{(\Delta E_{\text{elastic}}^{\delta\to\alpha'} + \Delta Q_{\text{plastic}}^{\delta\to\alpha'})}{\Delta S^{\alpha'\to\delta}} \quad \text{and} \quad A_s - T_0 \cong \frac{(\Delta E_{\text{elastic}}^{\alpha'\to\delta} + \Delta Q_{\text{plastic}}^{\alpha'\to\delta})}{\Delta S^{\alpha'\to\delta}}$$

For both the forward and reverse transformations, the heat is given by:

Q = TΔS



Inferred entropic change agrees well with previous observations

Away from equilibrium, the heat of transformation is a function of transformation temperature

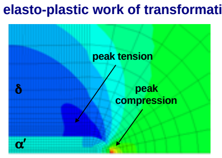
$$\Delta S = \frac{Q}{T} = \frac{\Delta H}{T}$$

	δ → α′	α′ → δ	Literature[1]
Q (J/mole)[2]	-717.8	3234	
T (°C)	-128	21	
T (K)	145	294	298
ΔS (J/mole·K)	-4.95	11	ΔS^0 = 11.6

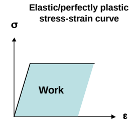
[1]Adler & Olson, Metall. Trans. (1988)
[2]Assuming 26% volume transformed to α′

We believe the δ → α′ transformation is incomplete during the cooling cycle, which lowers the ΔS estimate at low temperature

A finite element model is used to calculate the elasto-plastic work of transformation



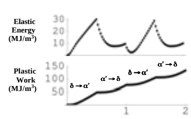
Elastic/perfectly plastic stress-strain curve



The 2D axisymmetric finite element model consists of a misfitting α′ plate in elastic/perfectly plastic delta matrix

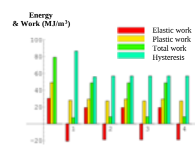
Comparison with available analytical solutions is good

Work to form α′ from δ is greater than the work to revert α′ into δ



Elastic energy (♦) is conserved in each cycle

Plastic work (★) continually increases



The model predicts a slightly greater hysteresis in the first cycle due to the development of a plastic zone

Initial FEM calculations of hysteresis are comparable to the experiment (~150 K)

$$\Delta T = \frac{W^{\delta\to\alpha'} + W^{\alpha'\to\delta}}{\Delta S^{\alpha'\to\delta}}$$

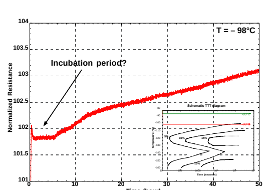
		Hysteresis (K)	
		Cycle 1	Cycle 2
Triaxial strain: $\varepsilon_x = \varepsilon_z = -0.0617$, $\varepsilon_y = -0.0964$			
	Sphere	168	131
	5:1 Slab	185	143
	40:1 Slab	229	168
Invariant plane strain: $\varepsilon_x = \varepsilon_z = 0.0$, $\varepsilon_y = -0.2044$			
	5:1 Slab	121	78
	40:1 Slab	14	7

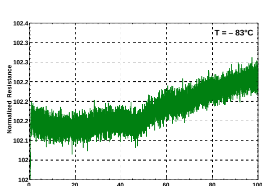
Results are sensitive to particle shape and transformation strain
Experimentally observed aspect ratio is ~20:1

Future work:
- Incremental growth of thin plate
- Finite size effects
- Work hardening

Ongoing and Future Work

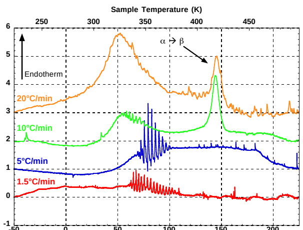
Isothermal annealing resistivity experiments indicate an incubation time before α′ begins to form





DSC is used to examine the effect of heating and cooling rates on the transformation

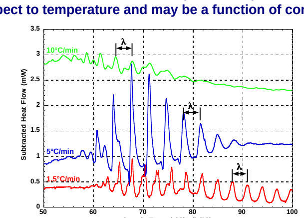
DSC thermogram: Heating

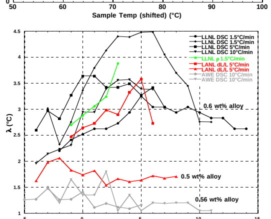


Unusual oscillations are seen during heating, but not on cooling

Oscillations have also been seen in DSC data obtained at the Atomic Weapons Establishment *(S. Kitching)* and Los Alamos *(D. Schwartz)* and in LANL dilatometry data *(J. Mitchell)*

The oscillations observed by DSC are periodic with respect to temperature and may be a function of composition





Period does not vary significantly with heating rate or characterization technique

Conclusions

For a 1.9 at% reference alloy…

- M_s and A_s temperatures (-120°C and 35°C, respectively) have been established using resistivity and differential scanning calorimetry
- A thermodynamic model involving plastic work was developed
  - ✧ ΔS calculated using the model and experimental results agrees with literature value (Adler and Olsen)
  - ✧ Modeling results of the hysteresis agree well with experiments
- Resistivity experiments indicate a possible incubation time before the formation of α′ begins
- "Oscillations" seen in DSC traces during the α′ → δ reversion are periodic with respect to temperature, not time
  - ✧ The period of "oscillations" seen by AWE and LANL in DSC and dilatometry correlate well with LLNL data

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